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Short communication

Sub/supercritical carbon dioxide induced phase switching for the reaction and separation in ILs/methanol

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Abstract

Separation of products from ionic liquid (IL) solvents is one of the main challenges that hinder their utilizations. In this study, the production of γ-valerolactone (GVL) by selective hydrogenation of α-angelica lactone (AL) and separation of the products from the IL solvent were carried out by using subcritical CO_2 as a "switch" at room temperature. After the mixture was separated into two phases by subcritical CO_2, AL and nano Pd/C catalyst were only found in the lower IL-rich phase, GVL was produced with quantitative yield and enriched in the upper methanol-rich phase. Pure GVL can be obtained by depressurizing to release CO_2 and evaporation to remove methanol of the upper phase, the lower phase containing IL, catalyst and methanol can be recycled for the next reaction. The strategy may provide a new approach to produce and separate products from IL solvents at mild conditions.

Keywords: Separation; Ionic liquids; Selective hydrogenation; Mild condition; Subcritical CO_2

1. Introduction

The major biomass components, cellulose and hemicelluloses, can be converted into various chemicals and fuels including sugars, ethanol, butanol, ethylene glycol, 5-(Hydroxymethyl)furfural, dimethylfuran and so on [1–10]. Among these biomass derived chemicals, γ-valerolactone (GVL) was paid special attention [11–14]. Horvath et al. [15] demonstrated that the biomass-derived compound γ-valerolactone can be used as solvent and fuel additives due to its several very attractive physical and chemical properties. GVL also can be converted into valuable chemicals including 1,4-pentanediols, dimethyl adipate, methyl pentenoate, 2-MeTHF, butene, pentenoic acid and so on [16]. Recently, Dumesic et al. introduced a strategy to produce soluble carbohydrates from corn stover, hardwood and softwood at high yields (70–90%) with the aid of GVL by promoting thermocatalytic saccharification through complete solubilization of the biomass, even including the lignin fraction [17]. In our previous studies, we also converted GVL into high octane number gasoline [18]. However, the industrial production of GVL has not been realized due to high cost and harsh reaction conditions.

There are several pathways to produce GVL, hydrogenation of levulinic acid (LA) to γ-hydroxyvaleric acid and followed by ring-closing and dehydration, hydrogenation of levulinate to make the hydroxy levulinic ester and further intramolecular transesterification [12,19–21]. For example, LA/water solution with a yield higher than 95% was obtained with $Ru(acac)_3$/TPPTS catalyst at 140 °C and 10 MPa for 12 h [20]. Tang et al. reported a green and efficient method for the conversion of ethyl levulinate into GVL by supercritical ethanol as the hydrogen donor and a good GVL yield of 82% was achieved at 250 °C [22]. Recently, many types of efficient

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catalysts were developed for the hydrogenation reaction [23−31]. Although these pathways are well-established and their conversions and yields are attractive, effective reduction of LA at mild conditions is proven to be difficult. We developed an efficient route for the production of GVL by hydrogenation of α-angelica lactone (AL) that can be produced by dehydration of LA with solid acid catalyst with high yield using a series of room-temperature ionic liquids (ILs) as the reaction solvents at room temperature [32−34]. Furthermore, the reaction system of IL/catalyst showed a good reusability, there was no decrease in conversion and selectivity after 10 cycles [34].

However, the commonly employed approaches for the separation of the final products from the ILs solvents are still difficult. Since most ILs are non-volatile [35−37], evaporation or distillation of the other components in the ILs is a feasible option, but evaporation and distillation are not practical for high-boiling or thermally unstable compounds and they also consume a lot of energy [38]. The other choice for the separation is extraction, but extraction by other organic solvents may cause cross contaminations between extractors and products and deteriorate the reusability of the catalysts and the solvents. Followed by the pioneer work by Brennecke et al. [38−43], many reactions were carried out by employing ILs and supercritical CO_2 systems, which achieved either high selectivity or efficient separations by supercritical CO_2 extraction [44−54]. Due to the non-polar of supercritical CO_2, it is not able to dissolve compounds with high polarity like GVL. Herein, we report a highly efficient catalytic system for the hydrogenation and separation in a biphasic system employing sub/supercritical CO_2 as a phase separation "switch", in which, both reaction and separation can be carried out in the same system operated in batch type or continuous type at room temperature. As shown in Fig. 1, the hydrogenation of AL to GVL can be carried out in 1-butyl-3-methylimidazolium hexafluorophosphate ($BmimPF_6$)/methanol solution at room temperature catalyzed by nano Pd/C catalyst (Fig. 1a). After the reaction, CO_2 is introduced to form a biphasic system (Fig. 1b). Once biphasic system is formed, the upper phase only contains methanol, GVL and CO_2, high purity GVL can be obtained by releasing pressure and evaporation of methanol at low temperature; while the lower phase contains a part of GVL, catalyst and methanol that can be recycled for the next reaction. The system also can be operated continuously as show in Fig. 1c. AL is selectively hydrogenated to produce GLV continuously. AL is favorably distributed in lower phase (AL concentration in lower phase: AL concentration in upper phase>99) and Pd/C catalyst also only can be found in the lower phase. GVL can be obtained by continuous removal of upper phase and separating CO_2, methanol and H_2 easily. Besides, such system also can be utilized to recycle or concentrate products from ILs system after the reaction, to carry out phase separation reactions, and for separations, including reactive separations. This *in-situ* reaction, separation and recycling method may address the limitations of the conventional evaporation, extraction, filtration and centrifugation in the presence of ILs.

2. Experimental

2.1. Materials

α-angelica lactone (97.0%) was obtained from Chifei Chemical Company and placed in a refrigerator at −20 °C to avoid isomerization to its β form (β-AL). $PdCl_2$ was purchased from J&K Scientific Ltd. Hydrochloric acid (38 wt%) was purchased from Xilong Chemical without further treatment. High purity gases, H_2, CO_2 and N_2 (99.99%) were obtained from Beiwen Special Gas Factory, $BmimBF_6$ (Chengjie, Shanghai, 99.0%) were placed in a vacuum oven at 60 °C to avoid water uptake before use. Methanol, γ-valerolactone in analytical purity were purchased from J&K Scientific Ltd and used as the standards without any further purification. HPLC grade Acetonitrile was provided by Fisher scientific, and distilled water was obtained from Watsons, Beijing.

2.2. Catalyst preparation

Pd/C catalyst was prepared by impregnation method on the activated carbon support with a 0.047 M H_2PdCl_4 solution. Activated carbon was coped with HNO_3 (30%) before use. According to theoretical calculations, a certain amount of H_2PdCl_4 solution was added into a flask containing 60 ml distilled water and 3.0 g activated carbon at 60 °C. Aqueous Na_2CO_3 solution (2 mol/L) was added into the impregnated solution to maintain constant pH. After stirred for 8 h, Pd precursor was reduced by using formaldehyde at 80 °C for 2 h. Then, the catalyst was washed with distilled water and dried at a vacuum oven for 18 h.

2.3. Selective hydrogenation

All reactions were carried out in a 50 ml high-pressure reactor with a safety relief and a pressure gauge. In a typical experiment run, 3 wt% catalyst (catalyst: α-AL), 5.0 g $BmimBF_6$, and 2.0 g (0.02 mol) α-AL were added to the reactor. The reactor was closed and air was flushed with N_2 at room temperature. H_2 and/or CO_2 were then charged into the reactor to designed pressure. The inlet value was closed and heated if needed with stirring to avoid settling of the catalyst. When the reaction was completed, upper and lower phases were sampled by a 1 ml sampler, CO_2 and H_2 were slowly released and weight of CO_2 was calculated by weight lose, the liquid compositions were analyzed by HPLC. Due to the low solubility of H_2 in both methanol and IL, composition of H_2 was not counted.

The products were analyzed by HPLC (Agilent 1100) equipped with a refractive index (RID) detector and an ODS-BP column (0.46 × 250 mm). Acetonitrile and water with a ratio of 3:7 was used as the mobile phase. The mobile phase was sonicated for 30 min before use. The oven temperature were set at 40 °C with a flow rate of 0.8 ml/min.

3. Results and discussion

Methanol and $BmimPF_6$ are completely miscible in any proportions at room temperature [55]. We firstly carried out

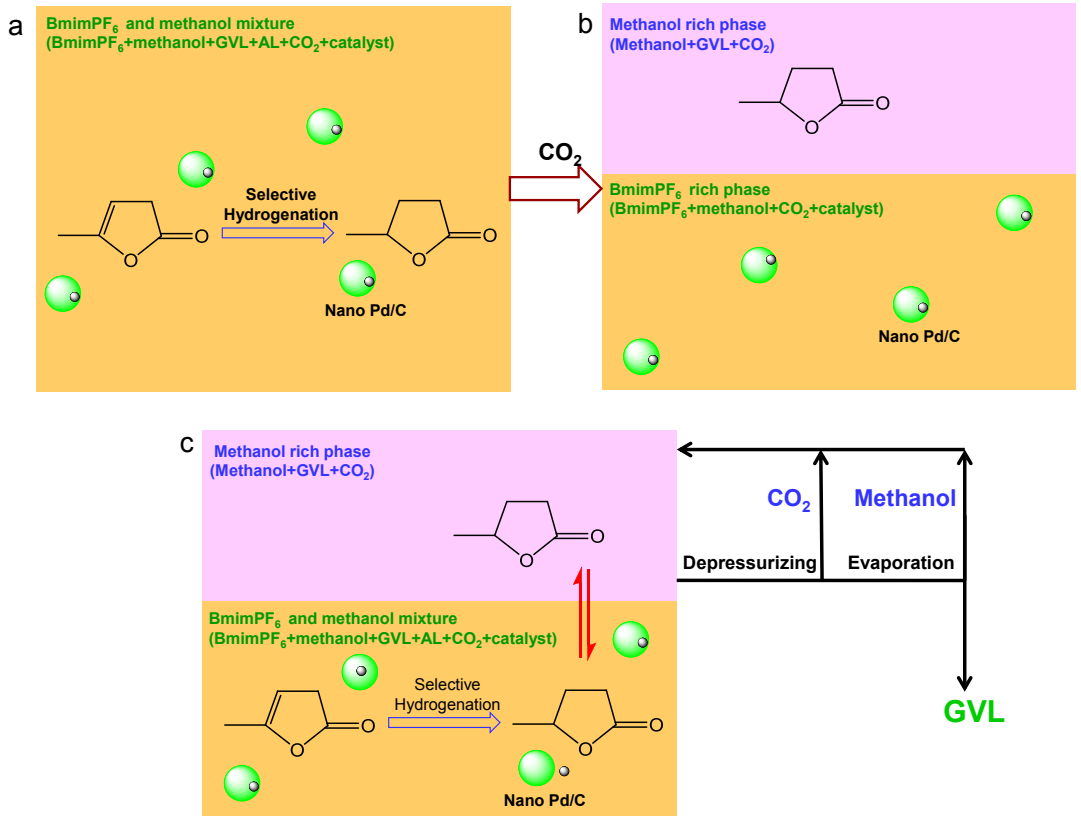

Fig. 1. a) Selective hydrogenation of AL to GVL with nano Pd/C as the catalyst; b) The mixture $BmimBF_6$/methanol + GVL and catalyst is separated into two phases induced by sub/supercritical CO_2 (>6.0 MPa); c) *In-situ* selective hydrogenation of AL to GVL in biphasic system induced by sub/supercritical CO_2 (>6 MPa).

the hydrogenation of AL to GVL in $BmimPF_6$/methanol with nano Pd/C as the catalyst at low temperature. As shown in Fig. 2, the reaction rate is rather fast even at room temperature; fully conversions of AL are achieved with 20 min and 30 min at 40 °C and room temperature respectively. It is found that the reaction rate is higher compared with our previous study [34]. The main reason is that the viscosity of $BmimPF_6$ is higher than that of methanol [56,57], the addition of methanol prompts the mass transfer.

After the reaction was completed, CO_2 was pumped to induce a separation of the mixture of $BmimPF_6$+methanol + GVL + Pd/C catalyst system. As we expected, the mixture formed a biphasic system at pressure higher than 6.0 MPa (Table 1). For all pressures, there was no detectable $BmimPF_6$ in the upper phase, indicating that the solubility of $BmimPF_6$ in the upper phase is lower than the determination limit of HPLC, which is similar to that reported before [55]. This is not surprising because the solubility of the IL in CO_2 is extremely low [58,59] and the methanol in the upper phase did not increase the solubility of IL in methanol + CO_2. In another word, the methanol in the upper phase cannot improve the solvent power of the CO_2 and it is further concluded that the upper phase contains only GVL, methanol and CO_2. Many researches proved that there are strong interactions between CO_2 and ILs that results in high CO_2

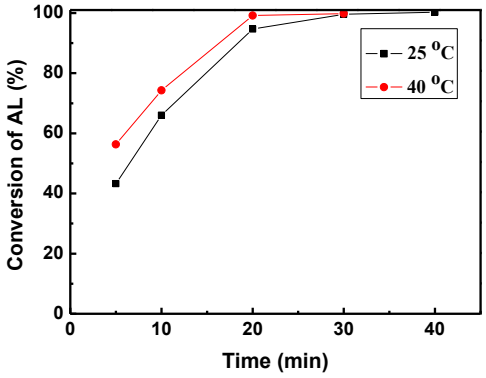

Fig. 2. Selective hydrogenation of AL to GVL at 25 °C and 40 °C. Reaction conditions: 4.0 MPa H_2, 2.0 g (0.02 mol) α-AL, 5.0 g (0.0176 mol) $BmimPF_6$, 8.7 g (0.275 mol) methanol, 10% Pd/C: 0.06 g (3 wt% of AL).

Table 1
Composition (mol%) of upper phase and lower phase induced by CO_2 at various pressures[a,b].

CO_2/Mpa	X_{GVL}		$X_{Methanol}$		X_{ILs}		X_{CO2}	
	Upper	Lower	Upper	Lower	Upper	Lower	Upper	Lower
6.0	0.0451	0.0590	0.1891	0.0370	0	0.1494	0.7658	0.7546
8.0	0.0392	0.0522	0.1584	0.0396	0	0.1020	0.8023	0.8062
10.0	0.0265	0.0482	0.1305	0.0903	0	0.0744	0.8431	0.7872
12.1	0.0250	0.0189	0.1694	0.0335	0	0.0315	0.8056	0.9162

[a] Conditions: 25 °C, standing for 2 h, 2.0 g GVL (0.02 mol), 5.0 g (0.0176 mol) $BmimPF_6$, 8.7 g (0.275 mol) methanol.
[b] See Table S2 for composition in wt%.

solubility in $BmimPF_6$ [59], but CO_2 is non-polar and not capable of dissolving $BmimPF_6$ [60]. Conversely, methanol is high polar, protic and possesses the ability to solvate ions. As CO_2 is dissolved in the upper phase, the solution expands substantially and the mixture of methanol/CO_2 is no longer a good solvent for $BmimPF_6$. Due to the gaseous nature of CO_2 and low boiling point of methanol under atmospheric pressure, pure GVL can be obtained by simply release the pressure and evaporation of methanol from the upper phase. If evaporation of methanol is carried out under negative pressure, the temperature employed can be as low as room temperature. The low separation temperature is extremely useful for the thermally unstable compounds and the bioactive organic compounds [61,62].

It is also seen from Table 1 that the fraction of CO_2 in the lower phase increased with the increase of pressure while that in the upper phase did change greatly. Both fractions of GVL in the upper phase and the lower phase decreased with the increase of pressure. However, the fraction ratio of GVL in the upper phase and the lower phase was 0.76 at 6.0 MPa, which increased to 1.32 at 12.1 MPa, indicating that partition coefficient was improved at higher CO_2 pressure. As we mentioned before that GLV is polar and CO_2 is non-polar, the increase of CO_2 fraction in $BmimPF_6$ at high pressure makes the GLV moving to the upper phase containing much methanol with high polarity, thus leads to higher partition coefficient.

In-situ reaction and separation also can be carried out simultaneously as shown in Fig. 1c. Before the reaction, 2.082 g (0.021 mol) AL, 5.0 g $BmimPF_6$ (0.0176 mol), 8.7 g (0.275 mol) methanol and 0.06 g 10% Pd/C catalyst were mixed and subjected into the reactor, 6.0 MPa of CO_2 was pumped to form a biphasic system and stabilized for 30 min. Then 4 MPa H_2 was pumped to start the selective hydrogenation. AL and GLV distribution and AL conversion and GVL selectivity are listed in Table 2. It is seen that the reaction rate was rather quick at the first 2 h, the conversion of AL reached 74%. After a reaction time of 5 h, AL was completely converted and quantitative yield of GVL was produced. More than half of the produced GVL distributed in the upper phase and the highest partition coefficient was 1.85 (Table 2, entry 4). For all reaction times, AL and Pd/C catalyst were only found in the lower phase, which ensured that the hydrogenation reaction only took place at the lower phase. One of the attractive merits of this behavior is that a part of the product is no longer contacting with the catalyst, which decreases the possibility of further reactions. Furthermore, if the reaction is an equilibrium reaction, the removal of the final products shifts the reaction to product side leading to higher yield.

Table 2
In-situ selective hydrogenation of AL to GVL catalyzed by Pd/C[a].

Entry	t (h)	AL_{upper} (%)	AL_{lower} (%)	GVL_{upper} (%)	GVL_{lower} (%)	AL con. (%)	GVL Sel.(%)
1	0.5	0	60	63	37	40	99
2	2	0	26	58	42	74	99
3	3	0	15	62	38	85	99
4	5	0	0	65	35	100	99

[a] Conditions: 2.082 g (0.021 mol) AL, 5.0 g $BmimPF_6$ (0.0176 mol), 8.7 g (0.275 mol) methanol and 0.06 g 10% Pd/C, 25 °C, 6.0 MPa CO_2 for 0.5 h and then 4.0 MPa H_2 was pumped.

We also studied the effects of CO_2 and H_2 pressures on the conversion of AL and the results are summarized in Table 3. At constant H_2 pressure (Entry 1−4, Table 3), the increase of CO_2 pressure from 2.4 MPa to 4.0 MPa changed the mixture from one-phase to two-phase. However, the increase of CO_2 pressure decreased the conversion of AL possibility due to that much CO_2 added diluted the concentration of AL and the catalyst. On the contrary, at constant CO_2 pressure (Entry 5−8, Table 3), the increase of H_2 pressure changed the mixture from two-phase to one-phase, indicating that high H_2 pressure prevents the formation of biphasic system. The simple explanation for our observations is that the solubility of CO_2 in the methanol/IL mixture is highly correlated with the pressure [39,43,58]. The solubility of CO_2 in $BmimPF_6$ is 0.27 g/g at 4 MPa and 40 °C, while the solubility increases 2 times to 0.57 g/g at 10 MPa [63]. When H_2 was introduced into the reactor, the total pressure was subsequently increased; much CO_2 in the upper phase was transferred and dissolved in the lower phase. Therefore the biphasic system integrated to single phase system. Regardless the phase behavior, high H_2 pressure is favored for the selective hydrogenation, a H_2 pressure of 2.0 MPa gave a conversion of 15% (entry 5, Table 3), the value increased to 69% when H_2 pressure was increased to 8.2 MPa (entry 8, Table 3).

4. Conclusions

In conclusion, we demonstrate here that the final products can be efficiently separated from the IL solvent by using CO_2 as a separation "switch" for the selective hydrogenation of AL to GVL in ($BmimPF_6$)/methanol at room temperature. In the batch-type process, the raw material AL and nano Pd/C catalyst only can be found in the lower phase and GVL is enriched in the upper phase. High purity GVL can be obtained from the upper phase by releasing pressure to remove CO_2 and evaporation of methanol at low temperature, the lower phase containing IL, catalyst and methanol can be recycled for the next reaction. In the *in-situ* reaction and separation process, the AL in the lower phase is continuously hydrogenated into GVL and extracted to the upper phase. The research provides a new method to carry out the reaction and separate the products, catalysts and IL solvents without using solvent extraction, evaporation that may contaminate or deteriorate the product or reaction solvent.

Table 3
Effects of H_2 and CO_2 pressures on the phase behavior and the conversion of Al[a].

Entry	P_{H2} (MPa)	P_{CO2} (MPa)	Phase behavior	Conversion (%)
1	4.2	2.4	One	73
2	4.0	4.0	Two	65
3	4.2	6.0	Two	62
4	4.2	7.9	Two	58
5	2.0	4.0	Two	15
6	4.2	4.3	One	44
7	6.2	4.2	One	55
8	8.2	4.0	One	69

[a] Reaction conditions: 2.0 g (0.02 mol) AL, 5.0 g (0.0176 mol) $BmimPF_6$, 8.7 g (0.275 mol) methanol, 10% Pd/C: 0.06 g (3 wt %), 25 °C, 2 h.

Conflict of interests

The authors declare no conflict of interests.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.gee.2016.04.002

References

[1]. G.W. Huber, S. Iborra, A. Corma, Chem. Rev. 106 (2006) 4044−4098.
[2]. M.E. Zakrzewska, E. Bogel-Łukasik, R. Bogel-Łukasik, Chem. Rev. 111 (2010) 397−417.
[3]. M. Besson, P. Gallezot, C. Pinel, Chem. Rev. 114 (2013) 1827−1870.
[4]. A.J.J. Straathof, Chem. Rev. 114 (2013) 1871−1908.
[5]. J. Zakzeski, P.C.A. Bruijnincx, A.L. Jongerius, B.M. Weckhuysen, Chem. Rev. 110 (2010) 3552−3599.
[6]. D.M. Alonso, S.G. Wettstein, J.A. Dumesic, Chem. Soc. Rev. 41 (2012) 8075−8098.
[7]. P. Gallezot, Chem. Soc. Rev. 41 (2012) 1538−1558.
[8]. A.A. Koutinas, A. Vlysidis, D. Pleissner, N. Kopsahelis, I. Lopez Garcia, I.K. Kookos, S. Papanikolaou, T.H. Kwan, C.S.K. Lin, Chem. Soc. Rev. 43 (2014) 2587−2627.
[9]. C. Liu, H. Wang, A.M. Karim, J. Sun, Y. Wang, Chem. Soc. Rev. 43 (2014) 7457−7956.
[10]. S. Zhang, J. Sun, X. Zhang, J. Xin, Q. Miao, J. Wang, Chem. Soc. Rev. 43 (2014) 7838−7869.
[11]. L. Bui, H. Luo, W.R. Gunther, Y. Román-Leshkov, Angew. Chem. Int. Ed. 52 (2013) 8022−8025.
[12]. Z.-P. Yan, L. Lin, S. Liu, Energy & Fuels 23 (2009) 3853−3858.
[13]. J.Q. Bond, D. Wang, D.M. Alonso, J.A. Dumesic, J. Catal. 281 (2011) 290−299.
[14]. J.Q. Bond, D.M. Alonso, D. Wang, R.M. West, J.A. Dumesic, Science 327 (2010) 1110−1114.
[15]. I.T. Horvath, H. Mehdi, V. Fabos, L. Boda, L.T. Mika, Green Chem. 10 (2008) 238−242.
[16]. D.M. Alonso, S.G. Wettstein, J.A. Dumesic, Green Chem. 15 (2013) 584−595.
[17]. J.S. Luterbacher, J.M. Rand, D.M. Alonso, J. Han, J.T. Youngquist, C.T. Maravelias, B.F. Pfleger, J.A. Dumesic, Science 343 (2014) 277−280.
[18]. J. Xin, D. Yan, O. Ayodele, Z. Zhang, X. Lu, S. Zhang, Green Chem. 17 (2015) 1065−1070.
[19]. W.R.H. Wright, R. Palkovits, ChemSusChem 5 (2012) 1657−1667.
[20]. H. Mehdi, V. Fábos, R. Tuba, A. Bodor, L. Mika, I. Horváth, Top. Catal. 48 (2008) 49−54.
[21]. A.M.R. Galletti, C. Antonetti, V. De Luise, M. Martinelli, Green Chem. 14 (2012) 688−694.
[22]. X. Tang, L. Hu, Y. Sun, G. Zhao, W. Hao, L. Lin, RSC Adv. 3 (2013) 10277−10284.
[23]. F. Liguori, C. Moreno-Marrodan, P. Barbaro, Acs Catal. 5 (2015) 1882−1894.
[24]. A.D. Chowdhury, R. Jackstell, M. Beller, ChemCatChem 6 (2014) 3360−3365.
[25]. J. Tan, J. Cui, T. Deng, X. Cui, G. Ding, Y. Zhu, Y. Li, ChemCatChem 7 (2015) 508−512.
[26]. G. Metzker, A.C.B. Burtoloso, Chem. Commun. 51 (2015) 14199−14202.
[27]. W. Fang, H. Sixta, ChemSusChem 8 (2015) 73−76.
[28]. A.M. Ruppert, J. Grams, M. Jedrzejczyk, J. Matras-Michalska, N. Keller, K. Ostojska, P. Sautet, ChemSusChem 8 (2015) 1538−1547.
[29]. X. Tang, Z. Li, X. Zeng, Y. Jiang, S. Liu, T. Lei, Y. Sun, L. Lin, ChemSusChem 8 (2015) 1601−1607.
[30]. A. Villa, M. Schiavoni, C.E. Chan-Thaw, P.F. Fulvio, R.T. Mayes, S. Dai, K.L. More, G.M. Veith, L. Prati, ChemSusChem 8 (2015) 2520−2528.
[31]. W. Luo, M. Sankar, A.M. Beale, Q. He, C.J. Kiely, P.C.A. Bruijnincx, B.M. Weckhuysen, Nat. Commun. 6 (2015).
[32]. J. Xin, S. Zhang, D. Yan, O. Ayodele, X. Lu, J. Wang, Green Chem. 16 (2014) 3589−3595.
[33]. M. Mascal, S. Dutta, I. Gandarias, Angew. Chem. Int. Ed. 53 (2014) 1854−1857.
[34]. R. Cao, J. Xin, Z. Zhang, Z. Liu, X. Lu, B. Ren, S. Zhang, ACS Sustain. Chem. Eng. 2 (2014) 902−909.
[35]. R. Ludwig, U. Kragl, Angew. Chem. Int. Ed. 46 (2007) 6582−6584.
[36]. D. Freudenmann, S. Wolf, M. Wolff, C. Feldmann, Angew. Chem. Int. Ed. 50 (2011) 11050−11060.
[37]. Z.-J. Chen, H.-W. Xi, K.H. Lim, J.-M. Lee, Angew. Chem. Int. Ed. 52 (2013) 13392−13396.
[38]. L.A. Blanchard, D. Hancu, E.J. Beckman, J.F. Brennecke, Nature 399 (1998) 28.
[39]. L.A. Blanchard, Z.Y. Gu, J.F. Brennecke, J. Phys. Chem. B 105 (2001) 2437−2444.
[40]. J.F. Brennecke, E.J. Maginn, AlChE J. 47 (2001) 2384−2389.
[41]. S. Aki, J.F. Brennecke, A. Samanta, Chem. Commun. (2001) 413−414.
[42]. L.A. Blanchard, J.F. Brennecke, Ind. Eng. Chem. Res. 40 (2001) 287−292.
[43]. J.L. Anthony, E.J. Maginn, J.F. Brennecke, J. Phys. Chem. B 106 (2002) 7315−7320.
[44]. B.R. Mellein, J.F. Brennecke, J. Phys. Chem. B 111 (2007) 4837−4843.
[45]. J. Zhang, B. Han, Acc. Chem. Res. 46 (2013) 425−433.
[46]. C.I. Melo, R. Bogel-Lukasik, E. Bogel-Lukasik, J. Supercrit. Fluids 61 (2012) 191−198.
[47]. R. Glaeser, Chem. Eng. Technol. 30 (2007) 557−568.
[48]. K. Burgemeister, G. Francio, V.H. Gego, L. Greiner, H. Hugl, W. Leitner, Chemistry-a Eur. J. 13 (2007) 2798−2804.
[49]. P. Wasserscheid, J. Industrial Eng. Chem. 13 (2007) 325−338.
[50]. L.C. Branco, A. Serbanovic, M.N. da Ponte, C.A.M. Afonso, Chem. Commun. (2005) 107−109.
[51]. Z.F. Zhang, W.Z. Wu, B.X. Han, T. Jiang, B. Wang, Z.M. Liu, J. Phys. Chem. B 109 (2005) 16176−16179.
[52]. M.T. Reetz, W. Wiesenhofer, G. Francio, W. Leitner, Adv. Synth. Catal. 345 (2003) 1221−1228.
[53]. P.B. Webb, D.J. Cole-Hamilton, Chem. Commun. (2004) 612−613.
[54]. W.Z. Wu, W.J. Li, B.X. Han, Z.F. Zhang, T. Jiang, Z.M. Liu, Green Chem. 7 (2005) 701−704.
[55]. A.M. Scurto, S.N.V.K. Aki, J.F. Brennecke, J. Am. Chem. Soc. 124 (2002) 10276−10277.
[56]. F. Jutz, J.-M. Andanson, A. Baiker, Chem. Rev. 111 (2010) 322−353.
[57]. J.P. Hallett, T. Welton, Chem. Rev. 111 (2011) 3508−3576.
[58]. C. Cadena, J.L. Anthony, J.K. Shah, T.I. Morrow, J.F. Brennecke, E.J. Maginn, J. Am. Chem. Soc. 126 (2004) 5300−5308.
[59]. X. Huang, C.J. Margulis, Y. Li, B.J. Berne, J. Am. Chem. Soc. 127 (2005) 17842−17851.
[60]. S.V. Dzyuba, R.A. Bartsch, Angew. Chem. Int. Ed. 42 (2003) 148−150.
[61]. S. Lancianesi, A. Palmieri, M. Petrini, Chem. Rev. 114 (2014) 7108−7149.
[62]. K. Tatsuta, S. Hosokawa, Chem. Rev. 105 (2005) 4707−4729.
[63]. Y. Gong, H. Wang, Y. Chen, X. Hu, A.-R. Ibrahim, A.-R. Tanyi, Y. Hong, Y. Su, J. Li, Ind. Eng. Chem. Res. 52 (2013) 3926−3932.